Application of iron chelates in hydrodesulphurisation

Wubs, Harm Jan

2. The kinetics of the oxidation of ferrous chelates of EDTA and HEDTA in aqueous solution.‡

2.1. Abstract.

The kinetics of the reaction of oxygen with ferrous chelates of EDTA and HEDTA were studied in a stirred cell reactor under industrial conditions. The temperature was varied from 20 °C to 60 °C and the concentration of the ferrous chelate ranged from 0 to 100 mole/m^3. The initial pH was 7.5. Under these conditions, the reaction appeared to be first order in oxygen and second order in ferrous chelate. The activation energy of the oxidation reaction is (27.2 ± 2.3) kJ/mole for the ferrous EDTA complex and (36.0 ± 1.1) kJ/mole for the HEDTA complex. At 25 °C, the rate constant k_{21} for Fe(II)HEDTA is 2.8×10^{-2} and for Fe(II)EDTA 6.5×10^{-2} m^6/mole^2 s. The diffusivity of these chelates (D_B) could be related to the diffusivity of oxygen (D_A) by $D_B/D_A = 0.183$. Contrary to expectations, the overall reaction stoichiometry was found to be less than 4 due to side-reactions. Generally, the overall reaction stoichiometry was between 3 and 4. An overall reaction model is presented that explains both the results of this work and earlier results from open literature. The following rate equation is derived from this model:

$$-R_B = \left(2+\nu_B^+\right)k_{39}\frac{1+\dfrac{k_{40}/k_{41}C_B}{1+k_{-40}C_P/k_{42}C_B}}{1+k_{-39}/k_{41}C_B+\dfrac{k_{40}/k_{41}C_B}{1+k_{-40}C_P/k_{42}C_B}}C_AC_B$$

with $\left(2+\nu_B^+\right)$ being the overall reaction stoichiometry.

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2.1. Introduction.

Many commercial processes are available for the removal of hydrogen sulphide from gaseous streams. Most of these processes use gas-liquid contactors in which the hydrogen sulphide is contacted with a reagent to give either another dissolved sulphide-containing component (e.g. alkanol-amine or hydroxide based processes) or elemental sulphur as a precipitate. Important representatives of the latter type are the so-called iron chelate based processes. The absorption with reaction of hydrogen sulphide with iron chelates is usually represented by:

$$\begin{aligned} &H_2S\,(g) &&\longleftrightarrow H_2S\,(aq) \\ &H_2S\,(aq) + 2\,Fe^{3+}Chelant^{n-} &&\longrightarrow S\downarrow + 2\,H^+ + 2\,Fe^{2+}Chelant^{n-} \end{aligned} \qquad (1)$$

In this equation, the number n denotes the charge of the chelant anion. Since the active ferric chelate is converted to inactive ferrous chelate, the latter component has to be regenerated into its ferric form by oxidation of the solution with oxygen. This reaction is usually represented by:

$$\begin{aligned} &O_2\,(g) &&\longleftrightarrow O_2(aq) \\ &O_2\,(aq) + 4\,Fe^{2+}Chelant^{n-} + 2\,H_2O &&\longrightarrow 4\,Fe^{3+}Chelant^{n-} + 4\,OH^- \end{aligned} \qquad (2)$$

This way, the iron chelate can be regarded as a pseudo catalyst in the reaction of hydrogen sulphide with oxygen (Buenger *et al.*, 1987). The sulphur that is produced is easily recoverable from the slurry. Another advantage of iron chelate based processes is that they essentially operate at ambient conditions, as illustrated in Table I.

Table I. Typical operation conditions of iron chelate based processes.

Temperature	20 - 60 °C
pH	6 - 9
Pressure	< 100 bar
Important chelants	EDTA, HEDTA, NTA
Iron chelate concentration	10 - 1000 mole/m^3
Chelant/iron ratio	1.1 - 1.6

Table II. Key characteristics of ferrous chelate oxidation studies from literature.

Authors	System[a]	Order		T, °C	pH	Ligand	Concentration in mole/m^3		
		O_2	Fe(II)				Fe(II)	Ligand	O_2
Zang & van Eldik, 1990	G II	1	1 - 2	15 - 50	2 - 7	EDTA, DTPA	0.025 - 20	0.05 - 20	0.125 - 1.25
			2			HEDTA			
Brown & Mazzarella, 1987	A IV	1	2	25	3 - 7	MIDA, PDTA, BDTA, DTPA	< 11.5	< 120	0.125 - 1.25
			1 - 2[b]			EDTA			
Sada *et al.*, 1987	A I	1	0.5	20 - 60	6 - 8	EDTA	< 20	< 40	0.018 - 0.064
			0.7	50		NTA			
Bull *et al.*, 1983	G II	1	1	25	7.6 - 11	EDTA	0.084[c]	0.1	0.27[c]
Travin & Skurlatov, 1981	G II	1	1	22	6	EDTA	0.1 - 0.2	0.1 - 10	0.25[c]
Purmal' *et al.*, 1980	H II	1	2 - 1	22	4.5 - 9	EDTA	0.05 - 5	0.055 - 5	0.125 - 0.25
Kurimura *et al.*, 1968	C, D II	1	1	25	2 - 7	EDTA, DTPA, HEDTA, NTA, EDTP, CyDTA	0.008 - 0.04	< 1.0	< 0.27
Tamura *et al.*, 1976	A VI	1	1	25	5.6 - 7	Chlorate, Nitrate, Sulphate, Halogenides	< 0.1	< 0.1	< 1.23
Kurimura *et al.*, 1969	E II	1	1	15 - 30	2 - 8	TTP	0.05 - 0.4	< 20	< 1.25
Stumm & Lee, 1961	A VI	1	1	5 - 35	6.6 - 7.4	Chlorate	< 0.1	100	0.12 - 0.25
Huffman & Davidson, 1956	C, D II	1	1	31	0 - 1.9	Sulphate	< 25	250 - 1000	< 1.23
			2	130-140					
Cher & Davidson, 1955	F III	1	1	20 - 30	1.1 - 1.8	Phosphate	< 20	200 - 800	0.1 - 1.23
George, 1954	A V	1	2	25 - 40	0 - 2.3	Chlorate	< 230	150 - 1.7×10^3	0.2 - 160
Lamb & Elder, 1931	E IV	1	2	30	-1 - 2	Sulphate	150 - 180	10 - 5×10^3	0.27[c]
This study	B III	1	2	20 - 60	7.5	EDTA, HEDTA	0 - 100	120	0.125 - 1.25

[a]) Experimental set-up: A) Bubble column; B) Stirred cell; C) Quartz cell with oxygen saturated liquid; D) Test tube; E) Stirred tank reactor; F) Shaken tank reactor; G) Stopped flow apparatus; H) 'Standing-jet' apparatus;
Method for rate determination: I) Chemical analysis of ferric iron; II) Photospectrometrical analysis of ferric chelate; III) Oxygen pressure indication; IV) Electro potential measurement; V) Colorimetry for ferric ions; VI) Chemical analysis of ferrous iron

[b]) depending on $[Fe(III)]_o$. [c]) not further specified.

2. *The kinetics of the oxidation of ferrous chelates of EDTA and HEDTA in aqueous solution.*

The regeneration of iron chelates is a key step in all these systems. Although much information is available, the actual data on kinetics and reaction velocities of the regeneration are very limited, see Table II for a summary. As may been seen from this Table, experiments have been carried out under both homogeneous and heterogeneous conditions, the latter being in line with the actual situation in industrial applications. Irrespective of the actual experimental conditions and the type of anion applied, i.e. a chelant such as EDTA or a more simple anion such as chloride, all authors agree that the oxidation rate of ferrous iron by molecular oxygen is first order in oxygen. The dependency of the oxidation rate on the concentration of ferrous iron, however, is more complicated. One group of authors found a first order dependency on ferrous iron whereas others found a second order dependency. With increasing concentrations even a change from first to second order has been observed (Zang and van Eldik, 1990; Brown and Mazzarella, 1987) or *vice versa* (Purmal' *et al.*, 1980). Considering these results, the approximately half order found by Sada *et al.* (1987) seems to be exceptional. These authors developed a model to explain both their own results and the results of Kurimura *et al.* (1968). In developing this model Sada *et al.* (1980) postulated that because $[O_2] << [Fe(II)]$, the first reaction step in which oxygen reacts with ferrous iron is zero order in Fe(II) and first order in oxygen. However, this postulate is unproved and seems questionable in light of the results of the other authors referred to in Table II. Amending this postulate results in a model that predicts a first order to second order dependency (see Brown and Mazzarella, 1987) which is in agreement with the results found by others.

Having established that the reaction order dependency on ferrous iron may vary from first to second order, the important question that remains is: under what circumstances is the reaction first order and under what conditions second order? Table II indicates that a change in order due to a change in pH seems to be unlikely. Bull *et al.* (1983), Travin and Skurlatov (1981) and Kurimura *et al.* (1968) all have measured a first order dependency with pH varying from 2 to 11. Also a second order dependency has been observed at the same pH range (Zang and van Eldik, 1990; Brown and Mazzarella, 1987; Purmal' *et al.*, 1980). Thus excluding pH, only the concentration of ferrous iron is left to explain the observed phenomena because both the experimentally applied temperature and the oxygen concentration were comparable. Comparing the experimentally observed reaction orders with the applied concentrations shows that all authors who reported a second order dependency used high ferrous iron concentrations whereas those

who found first order behaviour used low concentrations. This tendency can also be observed with simple anions present instead of chelants as EDTA or HEDTA (see for example: Huffman and Davidson, 1956; Lamb and Elder, 1931). In light of this, the results of Purmal' *et al.* (1980) seem contradictory to the suggested order dependency. Purmal' *et al.* (1980) found a decrease in reaction order with increasing ferrous iron concentration. However, because these authors based their conclusions on three data points only, their conclusion might be questionable. Nevertheless, the order found by them is also between one and two.

On comparison of the experimental conditions applied in the various kinetic investigations with the operational conditions applied in industrial iron chelate based desulphurisation plants, only Zang and van Eldik (1990) and Brown and Mazzarella (1987) have carried out some experiments under industrial conditions (shown in Table I), albeit only at very low ferrous chelate concentrations. Although both groups have measured up to a pH of 7, there is a general agreement that above a pH of about 6 the reaction is pH-independent (Zang and van Eldik, 1990; Sada *et al.*, 1987; Bull *et al.*, 1983; Travin and Skurlatov, 1981; Kurimura *et al.*, 1968).

To explain their results, Brown and Mazzarella (1987) developed the following reaction scheme:

$$Fe^{2+}L^{n-} + O_2 \xleftrightarrow{k_3, k_{-3}} Fe^{3+}L^{n-} + O_2^- \qquad (3)$$

$$Fe^{2+}L^{n-} + O_2^- \xrightarrow{k_4} Fe^{3+}L^{n-} + O_2^{2-} \qquad (4)$$

$$2\,H_2O + 2\,Fe^{2+}L^{n-} + O_2^{2-} \longrightarrow 2\,Fe^{3+}L^{n-} + 4\,OH^- \qquad (5)$$

Based on this mechanism and using the steady-state assumption with respect to the superoxide concentration they derived the rate expression:

$$-\frac{dC_{Fe^{2+}L^{n-}}}{dt} = \frac{4k_3k_4C_{O_2}C^2_{Fe^{2+}L^{n-}}}{k_{-3}C_{Fe^{3+}L^{n-}} + k_4C_{Fe^{2+}L^{n-}}} \qquad (6)$$

Clearly, this model is contradictory to the findings that at high ferrous iron concentrations the reaction is second order in ferrous iron and first order at low concentrations. Although eqn. (6) describes the findings of Brown and Mazzarella (1987) that with increasing ferric EDTA concentration the order dependency on ferrous EDTA changes from one to two, Travin and Skurlatov (1981) and Purmal' *et al.* (1980) concluded that ferric EDTA had no influence on the reaction kinetics. Further, also Brown and Mazzarella (1987) found no dependence on the ferric chelate concentration for several other chelants with the rate being predominantly second order in ferrous chelate. It may therefore be concluded that the above reaction scheme is not satisfactory and that the reported results need to be reinterpreted.

Very recently, Zang and van Eldik (1990) measured an increase of the kinetic order in ferrous chelate with increasing concentrations of ferrous chelate. To explain this behaviour, they proposed the following (reduced) reaction scheme:

$$Fe^{2+}L^{n-} + O_2 \longleftrightarrow Fe^{2+}O_2L^{n-} \quad (7)$$

$$Fe^{2+}O_2L^{n-} \longrightarrow Fe^{3+}L^{n-} + O_2^- \quad (8)$$

$$Fe^{2+}O_2L^{n-} + Fe^{2+}L^{n-} + 2\,H^+ \longrightarrow 2\,Fe^{3+}L^{n-} + H_2O_2 \quad (9)$$

$$Fe^{2+}L^{n-} + O_2^- + 2\,H^+ \longrightarrow Fe^{3+}L^{n-} + H_2O_2 \quad (10)$$

$$2\,Fe^{2+}L^{n-} + H_2O_2 + 2\,H^+ \longrightarrow 2\,Fe^{3+}L^{n-} + 2\,H_2O \quad (11)$$

At low concentrations of ferrous chelate, the first reaction step (eqn. 7) may be rate controlling with the third step (eqn. 9) still negligible. With increasing concentrations, however, the influence of the third reaction step (eqn. 9) may become more and more visible, finally overruling the second reaction step (eqn. 8) and thus changing the order from one to two. Therefore this reaction scheme of Zang and van Eldik (1990) seems most promising although their experimental conditions are rather different from operational conditions as typically encountered in industrial plants. Zang and van Eldik (1990) did not further incorporate above mechanistic scheme into an overall rate equation.

It is the aim of this work to establish the reaction kinetics at ferrous iron concentrations that are relevant to the industrial processes, i.e. for $10 < [Fe(II)] < 1000$ mole/m^3 compared to $0.025 < [Fe(II)] < 20$ mole/m^3 as used by Zang and van Eldik (1990). Both the ferrous iron order dependency and the reaction rate constants are reported. By carrying out experiments in a gas-liquid system under controlled conditions it turns out to be possible to obtain not only kinetic data but also data on the diffusivity of iron chelates, which is another relevant factor in calculating the mass transfer rate of oxygen and thus to the design of the regenerator. To our knowledge no open literature is available on the reactive absorption of oxygen in ferrous chelates under industrial conditions. Based on possible reactions taking place, a reaction kinetic model will be developed.

2.3. Experimental.

All kinetic experiments were carried out in a thermostatted reactor of glass and stainless steel (see Figure 1). A six bladed turbine stirrer was located centrally in the liquid at a height above the reactor bottom of half the reactor diameter. Four symmetrically mounted glass baffles increased the effectiveness of stirring and prevented the formation of a vortex. The reactor was operated at absolute pressures ranging from 20 mbar up to 950 mbar at various temperatures. The pressure and temperature transducers together with valves 1 and 2 were connected to an Olivetti M240 computer, thus enabling automatic data collection and programmed reactor operation. The operating conditions and the dimensions of the reactor are given in Tables III and IV, respectively.

Standard liquid reagent was made by dissolving $Na_2H_2EDTA\text{-}2H_2O$ or $Na_3HEDTA\text{-}2H_2O$ in 200 ml. water (reverse osmosis quality) in a 1 litre flask and adding 4 kmole/m^3 sodium or potassium hydroxide solution until a pH of 9 to 10 was reached. Once the solution was clear, oxygen was removed from the atmosphere above the liquid by continuously purging with N_2. Then $FeCl_2\text{-}2H_2O$ was added which gave the solution a clear, greenish appearance and a pH of about 2.5. After diluting to 900 ml., the pH was carefully brought to 7.5 and water was added up to 1 litre of solution.

The bulk of the solution was fed to the reactor under continuously purging with nitrogen. Subsequently, a sample of the liquid was taken to analyse the initial amount of

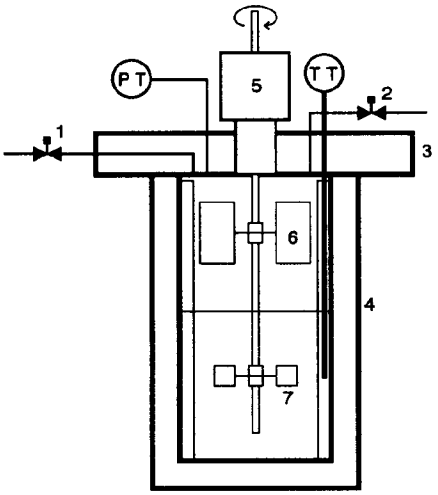

Figure 1. Stirred cell reactor.
1,2: computer activated valves
3: thermostatted stainless steel top
4: thermostatted glass reactor wall
5: Medimex magnetic coupling
6: gas stirrer
7: liquid stirrer

Fe(III) formed due to oxidation after which the gas cap of the reactor was evacuated. After the water vapour pressure had established, oxygen was supplied to the reactor through valve 1. The moment valve 1 opened was taken as $t = 0$. Typically, less than 5 seconds passed before the pre-set maximum experimental pressure was reached

Table III. Experimental conditions.

Temperature	20 - 60 °C
Absolute pressure	20 - 950 mbar
Liquid volume	8.57×10^{-4} - 9.50×10^{-4} m^3
Gas	O_2, purity > 99.5 %
	N_2O, purity > 99.5 %
Stirrer speed	200 - 600 rpm
initial pH	7.5

whereafter valve 1 closed and the stirrer was activated. Oxygen absorbed into the liquid resulted in a pressure decrease until a pre-set minimum experimental pressure was reached. Then some extra oxygen was supplied through valve 1 until the original pre-set maximum pressure was reached again. By repeating this procedure, a sawtooth curve was obtained (see Figure 2). As during the experiment $\Delta p << p$, p could be con-

sidered as constant. From each sawtooth $\Delta p/\Delta t$ was obtained at p and t through linear regression. Calculation of the regression coefficients of each $\Delta p/\Delta t$ indicated that the procedure was very accurate.

Table IV. Reactor dimensions.

Reactor diameter	0.105 m
Reactor volume	1.777×10^{-3} m^3
Gas-Liquid contact area	8.34×10^{-3} m^2
Liquid impeller type	six bladed turbine, 4 cm. dia.
Gas impeller type (optional)	six bladed turbine, 6 cm. dia. with enlarged blades

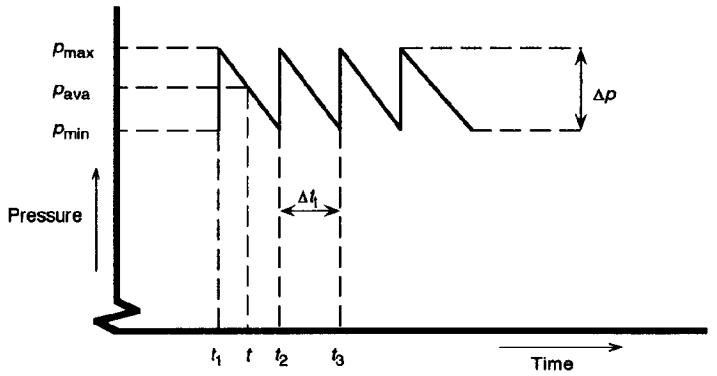

Figure 2. Schematic representation of the absorption procedure.

At the end of an oxygen absorption experiment, evacuation of the gas cap of the reactor brought the system under its own vapour pressure again. Subsequently N_2O was supplied to the reactor and after closing valve 1 and activating the stirrer, the pressure decrease due to physical absorption of N_2O was recorded over time, thus enabling the calculation of the liquid side mass transfer coefficient and the solubility of that gas. Both parameters turned out to be independent of the oxidation state of iron, see Table V.

Nitrous oxide rather than nitrogen was used to determine these parameters because using the latter would lead to larger errors due to its low solubility. Finally, the liquid was analysed for the amount of Fe(III) by adding an excess amount of potassium iodide to an acidified sample containing 25 ml. of ferric chelate solution. After the solution was allowed to stand in the dark for 1 hour under an atmosphere of carbon dioxide, the amount of iodine liberated due to the simultaneous conversion of ferric iron to ferrous iron and iodide to iodine was titrated with a 0.1 kmole/m^3 sodium thiosulphate solution.

Table V. Dependency of He and k_La on oxidation state of iron.
T = 294.6 K, pH = 8.1, $[Na^+]$ = 0.93 kmole/m^3;
$[Cl^-]$ = 0.60 kmole/m^3; $[HEDTA^{3-}]$ = 0.24 kmole/m^3.

$[Fe^{3+}]$ kmole/m^3	$[Fe^{2+}]$ kmole/m^3	*He* Pa m^3/mole	k_La s^{-1}
0.202		5021	2.27×10^{-3}
0.100	0.099	4847	2.07×10^{-3}
0.140	0.060	4910	2.18×10^{-3}
0.202		4864	2.14×10^{-3}

2.4. Gas solubilities and mass transfer coefficients.

The solubility of a gas in a liquid usually is expressed by the Henry-coefficient, which is defined as the ratio of the partial pressure of a gas and its equilibrium concentration in the liquid:

$$He = \frac{P}{C^l} \tag{12}$$

In absence of chemical reaction the concentration of the gas in the liquid follows directly from the total amount of gas absorbed. For an ideal gas:

$$He = \frac{p^\infty}{p^o - p^\infty} \cdot \frac{RTV_L}{V_G} \tag{13}$$

Figure 3 shows the experimentally obtained solubilities of N_2O in standard solutions of 100 mole Fe /m^3 used in this work (see Table VI for the composition of the respective EDTA and HEDTA iron complex solutions). This Figure also contains data on the solubility of N_2O in water as obtained by Versteeg and van Swaaij (1988). The solubilities of N_2O are correlated by:

HEDTA- solutions: $He = 7.71\times10^{6}\, e^{-2190/T}$ (14)

EDTA-solutions: $He = 7.51\times10^{6}\, e^{-2195/T}$ (15)

water: $He_0 = 1.15\times10^{7}\, e^{-2375/T}$ (16)

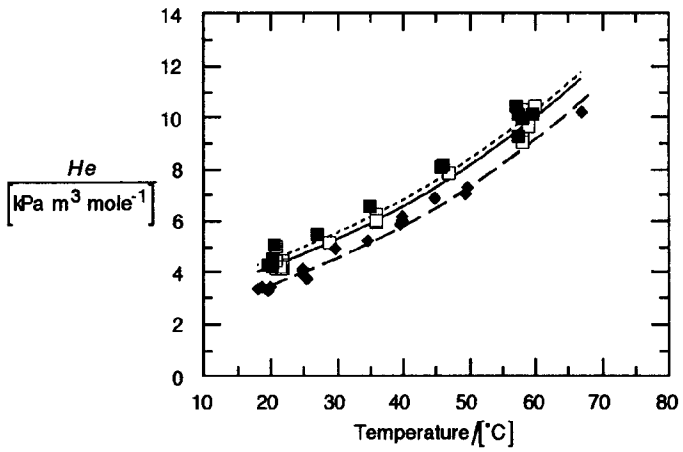

Figure 3. Solubility of N_2O in aqueous solutions of iron chelates of EDTA (□) and HEDTA (■) compared to the solubility in pure water (◆, Versteeg and van Swaaij, 1986). For the composition of the respective chelate solutions: see Table VI.
Lines : ..... eqn. (14); ——— eqn. (15); — — — eqn. (16).

The subscript 0 denotes the solubility in pure water. The average errors of eqns. (14) to (16) are about 3%. The solubility of oxygen in these solutions can be estimated with the model of Schumpe *et al.* (1978), who modified the salt-specific model of van

Krevelen and Hoftijzer (1948), which was later extended by Danckwerts (1970) for mixed salt solutions, into an ion-specific model:

$$\mathrm{Log}\left(\frac{He}{He_0}\right) = 0.5\sum_i H_i z_i^2 C_i \qquad (17)$$

in which H denotes the salting-out parameter, z the ion charge and C the concentration of species i. Although the salting-out parameters for the complexes present in our solutions are not known, a first estimate can be obtained by assuming:

$$z_i H_i = \text{constant for anions} \qquad (18)$$

Table VI. Basic constituents for FeEDTA and FeHEDTA complex solutions and comparison of the experimental (He/He_0) of nitrous oxide, obtained from eqn. (14) to (16), with the theoretical (He/He_0) of oxygen. The total chelant concentration was 0.12 kmole/m^3. pH = 7.5.

Solution with anion L is	Basic constituents [kmole/m^3]					(He/He_0)	
	K^+	Na^+	Cl^-	$Fe^{2+}L$	H^+L^a	25 °C	37 °C
$EDTA^{4-}$	0.216	0.240	0.200	0.100	0.020	1.20[b]	1.13[b]
$HEDTA^{3-}$		0.360	0.216	0.100	0.020	1.16[b]	1.17[b]
	Oxygen salting-out parameter H [m^3/kmole]						
ref.	K^+	Na^+	Cl^-	$Fe^{2+}L$	H^+L^a		
Schumpe *et al.* (1978)	-0.596	-0.550	0.884	0.45[c]	0.30[c]	1.19[e]	
				0.89[d]	0.45[d]	1.15[f]	
Lang and Zander (1986)	-0.013	0.000	0.257	0.15	0.10		1.16[e]
				0.30	0.15		1.12[f]

a). The amount of protonated ligand is calculated with the data of Sillén and Martell (1964, 1971).
b). Experimentally obtained for nitrous oxide, this work.
c). Estimated using eqn. (18); chelant is EDTA.
d). Idem; chelant is HEDTA.
e). Theoretical value for oxygen using eqn. (17); chelant is EDTA.
f). Idem; chelant is HEDTA.

Equation (18) is suggested from the salting-out parameters given by Schumpe *et al.* (1978) at 25 °C (agreement within 10%) and by Lang and Zander (1986) at 37 °C

(agreement within 15%). The solubility ratio He/He_0 thus calculated for oxygen is presented in Table VI and compared to the experimentally obtained solubility ratio He/He_0 for nitrous oxide. It appears that the theoretical and experimental values are the same within the experimental errors of eqns. (14) to (16). Therefore eqns. (14) to (16) provide a good alternative for calculating the oxygen solubility via:

$$\left(\frac{He}{He_0}\right)_{O_2} = \left(\frac{He}{He_0}\right)_{N_2O} \tag{19}$$

particularly because the effect of the temperature on the salting-out coefficients is not known but for the values given by Schumpe *et al.* (1978) and Lang and Zander (1986). The solubility of oxygen in pure water is given by Benson and Krause (1976).
Mass transfer coefficients were obtained from observing the physical absorption rate of nitrous oxide with time. The value of k_La follows from

$$\left(\frac{k}{k+1}\right)\ln\left(\frac{p_A^0}{(k+1)p_A - kp_A^0}\right) = k_L a t \quad \text{with} \quad k = \left(\frac{V_G He}{V_L RT}\right) \tag{20}$$

by linear regression techniques. The k_La thus found for N_2O is converted to k_La for oxygen using the relationship

$$(k_L a)_{O_2} = (k_L a)_{N_2O} \cdot \sqrt{\frac{D_{O_2}^{water}}{D_{N_2O}^{water}}} \tag{21}$$

The diffusivity of nitrous oxide in water is given by Versteeg and van Swaaij (1988) and the diffusivity of oxygen in water can be calculated, provided that the viscosity is expressed in poise instead of centipoise, by the relationship of St-Denis and Fell (1971), who related experimental diffusivities reported by other authors to T/η.

2.5. Results.

The absorption rate of oxygen, J_A, can be related to dp/dt through:

$$J_A a = \frac{V_G}{RTV_L} \cdot \left(-\frac{dp_A}{dt}\right) = \frac{V_G}{RTV_L} \cdot \left(-\frac{dp}{dt}\right) \tag{22}$$

The enhancement of the absorption of oxygen with respect to physical absorption is obtained from:

$$E_A = \frac{J_A}{k_L C_A^i} = \frac{1}{k_L a} \cdot \frac{He_A}{p_A} \cdot \frac{V_G}{RTV_L} \cdot \left(-\frac{dp_A}{dt}\right) \tag{23}$$

If $E_A > 1$, the absorption is chemically enhanced whereas $E_A < 1$ represents purely physical absorption of oxygen. The value of E_A is related to the amount of ferrous iron present in solution which in turn depends on the total amount of oxygen absorbed, N_A, via:

$$C_B = C_B^0 - \nu_B^o \cdot N_A \tag{24}$$

in which ν_B^o is the overall reaction stoichiometry, defined by the overall reaction

$$A + \nu_B^o B \longrightarrow \text{Products} \tag{25}$$

in which A stands for oxygen and B for the ferrous chelate. The quantity N_A is directly observed from experiment so that it is possible to present E_A as a function of C_B. Figure 4 shows some representative curves obtained in this manner for Fe(II)EDTA solutions assuming that ν_B^o is constant during each experiment. Fe(II)HEDTA solutions show the same characteristics. All the curves shown in Figure 4 are straight lines irrespective of the experimental conditions. Therefore the curvature does not depend on temperature, initial ferrous iron concentration or oxygen pressure. Also the lines obtained at an oxygen pressure of 91.3 kPa overlap despite the difference in initial ferrous chelate concentration. It therefore is concluded that the assumption of a constant ν_B^o during each experiment is valid. Substitution of eqn. (24) into eqns. (27) and (28) also shows that the observed linear dependency of E_A on N_A is only obtained if ν_B^o is constant.

Theoretically the relation between E_A and C_B depends on the regime of mass transfer with reaction that occurs. For a rate limiting reaction step

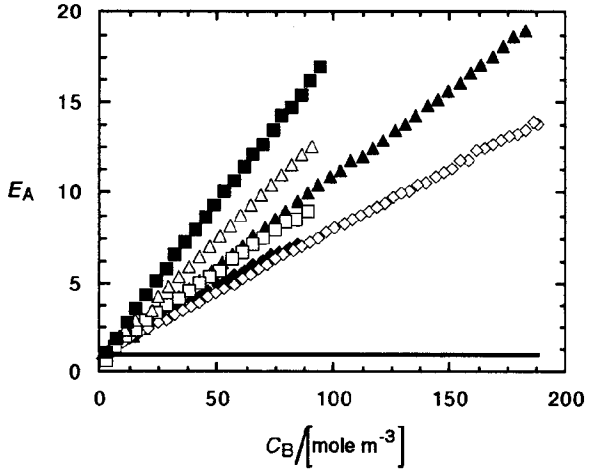

Figure 4. Enhancement factor of the absorption of oxygen for various temperatures, oxygen partial pressures and ferrous chelate concentrations. Chelant:iron ratio = 1.2. Initial ferrous chelate concentration = 100 mole/m^3. Legend: ■ 60 °C, 13.6 kPa; □ 50 °C, 83.8 kPa; ◆ 21 °C, 91.3 kPa; △ 21 °C, 13.4 kPa; ◇ 21 °C, 91.2 kPa; ▲ 21 °C, 43.1 kPa (◇, ▲ : initial ferrous chelate concentration = 200 mole/m^3); ——— $E_A = 1$.

$$A + \nu_B B \longrightarrow \text{Intermediates} \tag{26}$$

it can be derived that, in case of an instantaneous reaction, E_A is given by (Westerterp *et al.*,1984; see also the appendix of this chapter):

$$E_A = E_{A\infty} = 1 + \frac{D_B C_B}{\nu_B D_A C_A^i} \tag{27}$$

Equation (27) relates E_A proportionally to C_B and therefore an instantaneous reaction may well explain the results observed. In case of a chemically enhanced reaction with $E_{A\infty} >> Ha$, E_A is given by (Westerterp *et al.*, 1984):

$$E_A = Ha = \frac{1}{k_L} \cdot \sqrt{\frac{2}{q+1} D_A k_{pq} C_B^p C_A^{i\,q-1}} \qquad \text{for } 2 < E_A << E_{A\infty} \tag{28}$$

Here p and q are the reaction orders in ferrous iron and oxygen, respectively. The reaction of oxygen with ferrous iron is first order in oxygen (see Table II for literature results and Figure 5 for an example of our own experimental checks), therefore $q = 1$ and E_A does not depend on the concentration of oxygen at the gas-liquid interface as long as eqn. (28) holds. Above, it was pointed out that a linear relationship has been observed between E_A and C_B. If we are in the reaction regime $2 < E_A << E_{A\infty}$ then it follows from eqn. (28) that the reaction between oxygen and ferrous iron is second order in ferrous iron, which is in accordance with the results of Zang and van Eldik (1990). Equation (28) then reduces to:

$$E_A = Ha = \frac{1}{k_L} \cdot \sqrt{D_A k_{21}} \cdot C_B \tag{29}$$

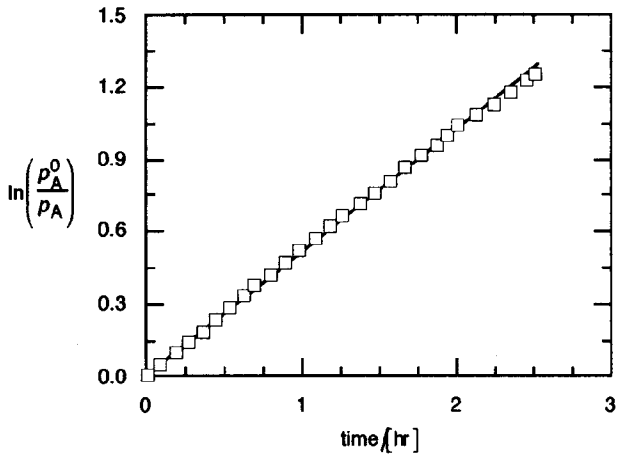

Figure 5. First order dependency on the concentration of oxygen. Temperature: 60 °C; Initial ferrous EDTA concentration: 100 mole/m^3. Chelant:iron ratio = 1.2.

From the curves of Figure 4 the slopes, i.e. dE_A/dC_B, can be calculated. From differentiating eqns. (27) and (29) to C_B, the two reaction regimes can be distinguished as follows:

instantaneous reaction regime:
$$C_A^i \frac{dE_A}{dC_B} = \frac{D_B}{\nu_B D_A} \tag{30}$$

chemically enhanced reaction regime:
$$C_A^i \frac{dE_A}{dC_B} = \frac{1}{k_L} \cdot \sqrt{D_A k_{21}} \cdot C_A^i \tag{31}$$

The results are presented in Figures 6 and 7. It is interesting to see that going from low interfacial oxygen concentrations toward high values, $C_A^i \, dE_A/dC_B$ first increases and then levels off to a constant value. According to eqn. (30), $C_A^i \, dE_A/dC_B$ must be independent of the oxygen concentration in the instantaneous reaction regime. This condition is apparently fulfilled at the high oxygen concentrations whereas at the low oxygen concentrations eqn. (31) is obeyed. It follows that the experiments have been carried out in the intermediate regime between instantaneous reaction and chemically enhanced absorption with $2 < E_A << E_{A\infty}$. Indeed, it was observed that by varying the stirrer speed at high oxygen concentrations, in contrast to effects observed on J_A, hardly any effects on E_A could be observed whereas at low oxygen concentrations the factor $k_L E_A$ was practically independent of stirring rate.

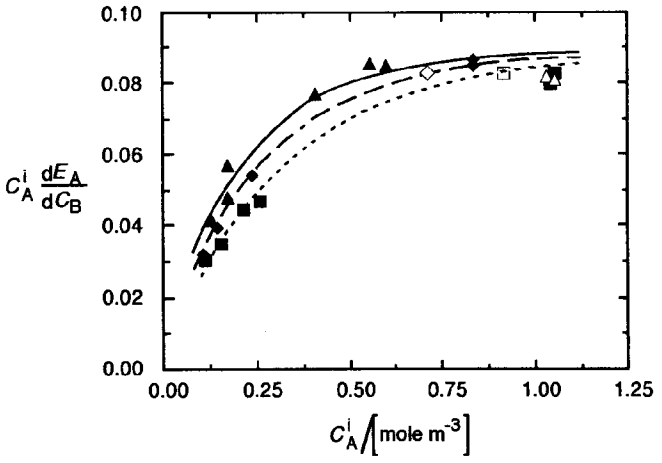

Figure 6. Determination of the reaction regimes for Fe(II)HEDTA solutions. Standard conditions: pH = 7.5; initial ferrous chelate concentration: 100 mole/m^3; ratio HEDTA/Fe = 1.2. Legend: ■ 21 °C; □ 29 °C; ◆ 36 °C; ◇ 47 °C; ▲ 59 °C; Δ 21 °C, HEDTA/Fe = 2-3; ..... eqn. (33), 21 °C; — — — eqn. (33), 36 °C; ——— eqn. (33), 59 °C.

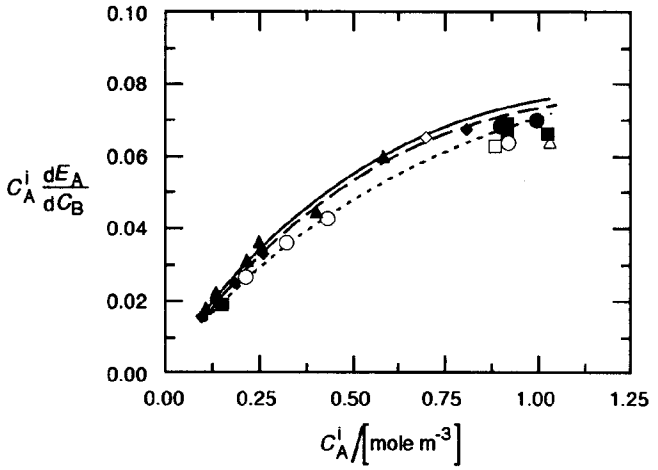

Figure 7. Determination of the reaction regimes for Fe(II)EDTA solutions. Standard conditions: pH = 7.5; initial ferrous chelate concentration: 100 mole/m^3; ratio EDTA/Fe = 1.2. Legend: ■ 20 °C; □ 27 °C; ◆ 36 °C; ◇ 46 °C; ▲ 58 °C; △ 20 °C, pH = 9; ● 20 °C, EDTA/Fe = 2-3; ○ 20 °C, [Fe] = 200 mole/m^3; ..... eqn. (33), 20 °C; — — — eqn. (33), 36 °C; ——— eqn. (33), 58 °C.

Several relations exist for E_A in this intermediate regime. Very practical is the explicit approximated relation of DeCoursey (1974):

$$E_A = -\frac{Ha^2}{2(E_{A\infty}-1)} + \sqrt{\frac{Ha^4}{4(E_{A\infty}-1)^2} + \frac{E_{A\infty}Ha^2}{(E_{A\infty}-1)} + 1} \qquad (32)$$

According to this model, E_A depends both on Ha and $E_{A\infty}$. Since under all conditions straight curves (as in Figure 4) are obtained for E_A as $f(C_B)$ irrespective of the reaction regime (see Figs. 6 and 7), Ha and $E_{A\infty}$ both must depend linearly on C_B, which can only be the case if the reaction is second order in the iron chelate, as pointed out above. For $Ha >> 1$ it follows from eqn. (32) that:

$$C_A^i \frac{dE_A}{dC_B} = \frac{PC_A^{i2}}{2Q}\left(\sqrt{1+\frac{4Q^2}{PC_A^{i2}}} - 1\right) \quad \text{with } P = \frac{k_{21}D_A}{k_L^2},\ Q = \frac{D_B}{\nu_B D_A} \qquad (33)$$

The maximum inaccuracy in eqn. (32) for reactions that are first order in both A and B is about 13 % for $D_B/D_A = 0.02$ and decreases to maximal errors of about 6 % for $D_B = D_A$ (DeCoursey, 1974).

The reaction between oxygen and ferrous iron being first order in oxygen and second in ferrous iron may well be understood by the reaction scheme given by Zang and van Eldik (1990) when reducing the first part to:

$$2\ Fe^{2+}L^{n-} + O_2 + 2\ H^+ \longrightarrow 2\ Fe^{3+}L^{n-} + H_2O_2 \qquad (34)$$

which is followed by a fast reaction between peroxide and ferrous iron. Effectively, eqn. (34), being the rate limiting step, is the reaction under study in the present work. In the following section this reaction will be discussed in more detail. The stoichiometric coefficient ν_B, being the stoichiometric coefficient of the rate limiting reaction step, therefore equals 2. The results thus obtained for the ratio of diffusivities and the reaction rate constants, calculated with equation (33), are presented in Table VII and Figure 8. Tables VIII and IX provide additional information on the parameters needed for this calculation.

Table VII. Kinetic parameters obtained from Figures 6 and 7 by applying eqn. (33). Data used for the calculation are based on: Fe = 100 mole/m^3; Ligand/Fe = 1.2; pH = 7.5.

	$Fe^{II}HEDTA$			$Fe^{II}EDTA$	
T	D_B/D_A	k_{21}	T	D_B/D_A	k_{21}
℃	-	m^6 / mole^2 s	℃	-	m^6 / mole^2 s
21	0.173	0.0225	20	0.182	0.0056
36	0.187	0.0482	36	0.188	0.0090
59	0.184	0.122	58	0.183	0.0200

Since using the model of DeCoursey (1974) leads to the product $D_A k_{21}$ rather than k_{21}, the value of D_A must be known to calculate k_{21}. As the diffusivity of oxygen in pure water is known, only a correction for viscosity needs to be applied. From viscosity experiments it appeared that for ferrous HEDTA solutions $\eta/\eta_0 = 1.39$ and for ferrous EDTA solutions $\eta/\eta_0 = 1.47$ under the experimental conditions used in this work (this

ratio was 1.79 for 200 mole ferrous EDTA per m^3). The influence of viscosity on oxygen diffusivities in aqueous electrolyte solutions was measured by Ho *et al.* (1988) and found to be given by $D\eta^{0.62}$ = constant.

Table VIII. Parameters for the determination of the diffusivity, D_B, and the reaction rate constant, k_{21}, of the ferrous chelate of HEDTA and comparison of the calculated value of $\left(C_A^i \frac{dE_A}{dC_B}\right)$ with the experimental value. The relative difference Δ is calculated as (exp-calc)/calc.

no.	T	$\frac{D_A}{k_L^2}$	C_A^i	$\left(C_A^i \frac{dE_A}{dC_B}\right)_{exp}$	$\left(C_A^i \frac{dE_A}{dC_B}\right)_{calc}$	Δ
	[K]	[s]	[mole/m^3]	[-]	[-]	[%]
1	294.3	5.29	1.044	0.0804	0.0863	-6.9
2	294.4	4.40	1.027	0.0814	0.0853	-4.5
3	294.2	2.72	1.052	0.0819	0.0825	-0.7
4	294.5	4.26	0.108	0.0297	0.0282	5.2
5	294.8	3.13	1.037	0.0787	0.0835	-5.7
6	294.8	3.65	0.255	0.0459	0.0502	-8.6
7	295.0	3.68	0.209	0.0437	0.0443	-1.4
8	295.0	3.78	0.152	0.0339	0.0357	-4.8
9	302.3	3.20	0.912	0.0815	0.0843	-3.4
10	308.9	2.51	0.831	0.0855	0.0835	2.3
11	308.9	2.91	0.102	0.0312	0.0306	2.1
12	309.0	2.27	0.829	0.0843	0.0828	1.8
13	309.1	2.66	0.234	0.0534	0.0532	0.5
14	309.1	2.62	0.138	0.0387	0.0372	4.1
15	320.4	2.19	0.706	0.0825	0.0838	-1.6
16	331.3	1.54	0.123	0.0407	0.0396	2.7
17	331.3	1.54	0.166	0.0469	0.0486	-3.5
18	332.3	1.93	0.594	0.0843	0.0839	0.5
19	332.4	1.91	0.406	0.076	0.0775	-1.9
20	332.5	2.07	0.553	0.0847	0.0835	1.5
21	332.8	1.95	0.170	0.0559	0.0541	3.4

The observed ratio D_B/D_A could be correlated for both ferrous EDTA and ferrous HEDTA complexes by the following empirical equation (see Table VII):

$$D_B/D_A = 0.183 \pm 0.005 \qquad (35)$$

Table IX. Parameters for the determination of the diffusivity, D_B, and the reaction rate constant, k_{21}, of the ferrous chelate of EDTA and comparison of the calculated value of $\left(C_A^i \frac{dE_A}{dC_B}\right)$ with the experimental value. The relative difference Δ is calculated as (exp-calc)/calc.

no.	T	$\frac{D_A}{k_L^2}$	C_A^i	$\left(C_A^i \frac{dE_A}{dC_B}\right)_{exp}$	$\left(C_A^i \frac{dE_A}{dC_B}\right)_{calc}$	Δ
	[K]	[s]	[mole/m^3]	[-]	[-]	[%]
1	293.4	3.56	0.918	0.0662	0.0666	-0.7
2	293.4	3.56	0.917	0.0686	0.0666	3.1
3	293.4	3.56	0.920	0.0633	0.0649	-2.6
4	293.4	3.56	0.435	0.0429	0.0419	2.2
5	293.4	3.56	0.434	0.0425	0.0419	1.7
6	293.4	3.56	0.323	0.0358	0.0336	6.3
7	293.4	3.56	0.214	0.0266	0.0241	10.7
8	293.5	3.26	1.000	0.0696	0.0679	2.5
9	293.5	3.15	1.032	0.0636	0.0682	-6.8
10	293.6	2.66	1.030	0.0662	0.0658	0.6
11	293.7	4.28	0.900	0.0681	0.0688	-1.0
12	294.8	3.59	0.149	0.0191	0.0190	0.4
13	300.2	2.67	0.884	0.0625	0.0650	-3.9
14	308.2	2.61	0.811	0.0670	0.0663	1.1
15	309.2	2.70	0.183	0.0252	0.0252	0.3
16	309.2	2.79	0.137	0.0198	0.0199	-0.3
17	309.2	2.86	0.099	0.0153	0.0150	1.9
18	309.4	2.88	0.263	0.0327	0.0347	-5.6
19	319.0	1.78	0.701	0.0647	0.0616	4.9
20	330.5	1.51	0.584	0.0598	0.0589	1.5
21	330.8	1.61	0.215	0.0313	0.0308	1.5
22	330.8	1.63	0.105	0.0176	0.0168	4.8
23	331.0	1.70	0.136	0.0221	0.0216	2.7
24	331.1	1.78	0.250	0.0360	0.0361	-0.5
25	331.3	1.40	0.403	0.0446	0.0467	-4.5

Figure 8 gives the respective Arrhenius plots of the reaction rate constant of Fe(II)HEDTA and Fe(II)EDTA with oxygen at standard conditions. The results are correlated according to

$$k_{21} = k_{21}^0 \, e^{-Ea/RT} \tag{36}$$

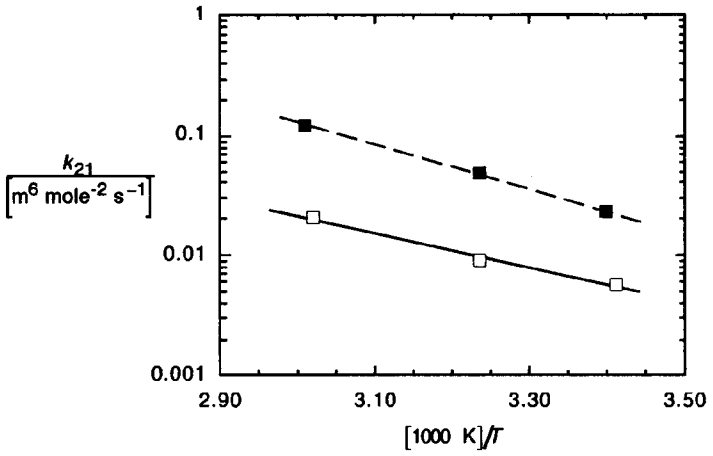

Figure 8. Temperature dependency of the rate constant k_{21}. Conditions: pH = 7.5, initial ferrous chelate concentration: 100 mole/m^3; ratio chelant/Fe = 1.2. Legend: ■ HEDTA; □ EDTA; _ _ _ eqn. (37), HEDTA; ——— eqn. (38), EDTA.

with:

$$\text{Fe(II)HEDTA}: \quad Ea = (36.0 \pm 1.1)\ \text{kJ/mole} \qquad k_{21}^0 = 5.8\times10^4\ \text{m}^6/\text{mole}^2\ \text{s} \qquad (37)$$

$$\text{Fe(II)EDTA}: \quad Ea = (27.2 \pm 2.3)\ \text{kJ/mole} \qquad k_{21}^0 = 3.8\times10^2\ \text{m}^6/\text{mole}^2\ \text{s} \qquad (38)$$

At 25 °C, k_{21} for Fe(II)HEDTA is 2.8×10^{-2} and for Fe(II)EDTA 6.5×10^{-3} m^6/mole^2 s. Tables VIII and IX show that equation (33) together with eqns. (35) to (38) predicts the measured data within an average error of about 3 %.

The values thus obtained can be compared with the results of Zang and van Eldik (1990). These authors found for the HEDTA complex an activation energy of (33.1±1.3) kJ/mole whereas they found for the EDTA complex an activation energy of (33.9±1.4) kJ/mole. At 25 °C the reaction rate constants reported by them were 9.77×10^{-2} and 1.51×10^{-2} m^6/mole^2 s respectively. The values for the reaction rate constants found in this work are qualitatively in good agreement with those reported by Zang and van Eldik (1990) although the absolute values are about a factor of 2 lower. This (relatively small) discrepancy may be ascribed to the very different methods used

in determining the reaction kinetics of chelated ferrous iron with oxygen. The heterogeneous method used in this work and the higher ferrous chelate concentrations applied are closer to actual industrial practice. Apart from the experimental methods used, another point is the possible effect of the data interpretation by Zang and van Eldik (1990) which, depending on the conditions applied, is not always justified. These authors translated their results into pseudo first order reaction rate constants, which is correct only when dealing with large differences in concentrations of oxygen and ferrous iron, i.e. $\frac{C_{Fe^{2+}L^{n-}}}{C_{O_2}} >> 1$ or $\frac{C_{Fe^{2+}L^{n-}}}{C_{O_2}} << 1$. However, these conditions are not fulfilled at the lower end of the plots Zang and van Eldik (1990) made for determining the reaction order in ferrous chelate. Also in determining the reaction order in oxygen, Zang and van Eldik (1990) assumed first order kinetics in ferrous iron, whereas they finally concluded that the reaction is second order in ferrous iron if complexated by HEDTA. Although Zang and van Eldik (1990) found the reaction to be first order in oxygen, the plots they made for the observed pseudo-first-order reaction rate constants versus the oxygen concentration show intercepts at zero oxygen concentration which significantly deviate from zero.

Finally, from curves such as those reported in Figure 4 the overall reaction stoichiometry is obtained by dividing the initial amount of ferrous iron present in solution by the total amount of oxygen absorbed at $E_A = 1$. Although it may be expected that the overall stoichiometry is 4 (reaction equation 2) as usually is thought (see for example: Kurimura *et al.*, 1968, Sada *et al.*, 1987 and Brown and Mazzarella, 1987) this is not the case, as can be seen from Figures 9 and 10. The overall reaction stoichiometries range between 3 and 4. This deviation is also reported by Burkitt and Gilbert (1991) who found for both ferrous EDTA and ferrous NTA complexes a stoichiometry of 3.3 at 37 °C and pH = 7.4. Note that the overall stoichiometry seems to depend both on temperature and oxygen solubility, thus probably on local reaction rates in the film. Tests revealed that the solutions did not have any ferrous iron oxidising capacity left and it was therefore concluded that the deviation of the overall stoichiometry was caused by a side reaction.

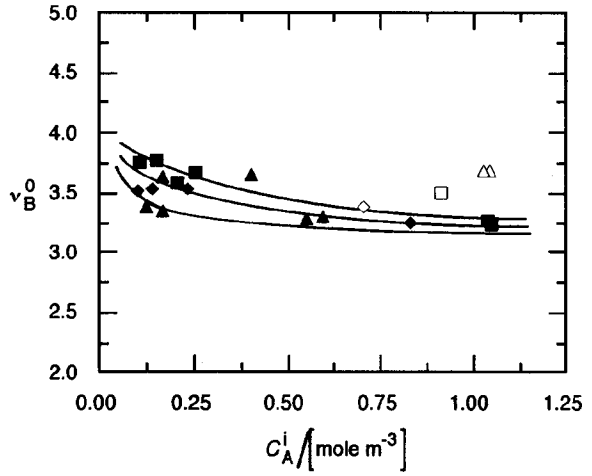

Figure 9. Overall reaction stoichiometry for Fe(II)HEDTA solutions as function of the oxygen solubility and temperature. Standard conditions: pH = 7.5; [Fe] = 100 mole/m^3; ratio HEDTA/Fe = 1.2. Legend: ■ 21 °C; □ 29 °C; ◆ 36 °C; ◇ 47 °C; ▲ 59 °C; △ 21 °C, HEDTA/Fe = 2-3.

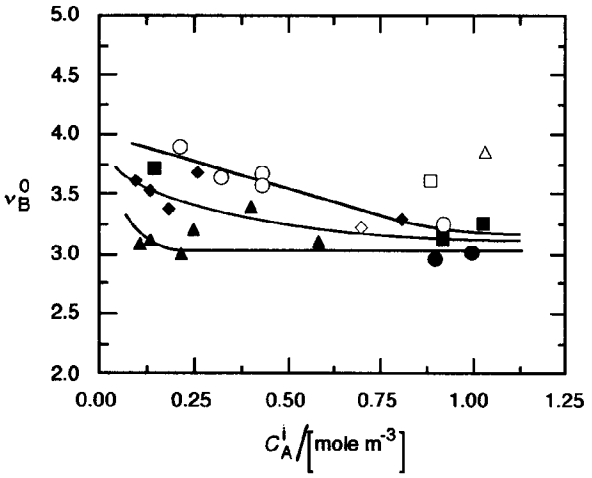

Figure 10. Overall reaction stoichiometry for Fe(II)EDTA solutions as function of the oxygen solubility and temperature. Standard conditions: pH = 7.5; [Fe] = 100 mole/m^3; ratio EDTA/Fe = 1.2. Legend: ■ 20 °C; □ 27 °C; ◆ 36 °C; ◇ 46 °C; ▲ 58 °C; △ 20 °C, pH = 9; ● 20 °C, EDTA/Fe = 2-3; ○ 20 °C, [Fe] = 200 mole/m^3.

In the next section a possible reaction scheme is presented that takes into account both first and second order dependencies on ferrous iron as well as a deviation of the overall stoichiometry from 4.

2.6. Discussion.

2.6.1. Diffusivities.

The results on diffusivities reveal that the diffusion coefficients of ferrous chelates follow the Stokes-Einstein relationship in that the ratio D_B/D_A is constant. No difference in the diffusivities of ferrous EDTA and ferrous HEDTA was observed. Also this result is as expected because of the very similar sizes of these complexes. At the pH of interest, the ferrous chelate species present in the solution are the normal, i.e. neither hydroxylated nor protonated, species (Clark and Martell, 1988) and therefore the ferrous EDTA species has a net charge of -2 and the ferrous HEDTA species a net charge of -1. Notably, these differences in complex charge are not reflected in diffusivity differences. Therefore the diffusivity of these species under the experimental conditions applied in this work is not related to charge but depends on size as is the case for uncharged species (see also the appendix of this chapter). The independence of charge is also illustrated by the tracer-diffusion coefficient of ferric EDTA. At 25 °C and pH = 7.9 this coefficient is 0.39×10^{-9} m^2/s (O'Conner *et al.*, 1971), with the ferric chelate species being entirely present in its monohydroxy form and having a net charge of -2. This compares very well with the diffusion coefficient of the ferrous EDTA and HEDTA found in this work, which was calculated as 0.42×10^{-9} m^2/s at 25 °C using the relationship that St-Denis and Fell (1971) found for the diffusivity of oxygen in water.

2.6.2. Reaction Kinetics.

Based on the references cited in Table II, including the investigations of Burkitt and Gilbert (1991), Cohen and Sinet (1980), Abel (1954), Weiss (1953), Butler and Halliwell (1982), Ilan and Czapski (1977), McClune *et al.* (1977), Orhanovic and

2. The kinetics of the oxidation of ferrous chelates of EDTA and HEDTA in aqueous solution.

Wilkins (1967), and Walling and co-workers (1970, 1975a,b) we conclude at the following possible reaction scheme:

$$Fe^{2+}L^{n-} + O_2 \xleftrightarrow[k_{-39}]{k_{39}} Fe^{2+}O_2L^{n-} \quad (39)$$

$$Fe^{2+}O_2L^{n-} \xleftrightarrow[k_{-40}]{k_{40}} Fe^{3+}L^{n-} + O_2^- \quad (40)$$

$$Fe^{2+}O_2L^{n-} + Fe^{2+}L^{n-} + 2\,H_2O \xrightarrow{k_{41}} 2\,Fe^{3+}L^{n-} + H_2O_2 + 2\,OH^- \quad (41)$$

$$Fe^{2+}L^{n-} + O_2^- + 2\,H_2O \xrightarrow{k_{42}} Fe^{3+}L^{n-} + H_2O_2 + 2\,OH^- \quad (42)$$

$$\nu_B^+\,Fe^{2+}L^{n-} + H_2O_2 + \left(2-\nu_B^+\right)OC \xrightarrow{fast} \nu_B^+\,Fe^{3+}L^{n-} + \nu_B^+\,OH^- + \left(2-\nu_B^+\right)DP \quad (43)$$

with: $1 \le \nu_B^+ \le 2$, OC = Organic Compound and DP = Degradation Product

These reactions are first order in the iron containing components, oxygen, superoxide and hydrogen peroxide and zero order in water and OC. Further, the equilibria that exist between hydroxide and ferric chelate should be included (Gustafson and Martell, 1963):

$$Fe^{3+}L^{n-} + OH^- \xleftrightarrow{K_A} Fe^{3+}(OH^-)L^{n-} \quad (44)$$

$$Fe^{3+}(OH^-)L^{n-} + OH^- \xleftrightarrow{K_B} Fe^{3+}(OH^-)_2L^{n-} \quad (45)$$

The monohydroxy species may form dimers according to:

$$2\,Fe^{3+}(OH^-)L^{n-} \xleftrightarrow{K_D} \left[Fe^{3+}(OH^-)L^{n-}\right]_2 \quad (46)$$

or alternatively:

$$2\ Fe^{3+}(OH^-)L^{n-} \quad \xleftrightarrow{K_D} \quad \left[Fe^{3+}L^{n-}\right]_2O + H_2O \tag{47}$$

which is the preferred reaction (Wilkins and Yelin, 1969). The dihydroxy form of ferric EDTA (see eqn. 45) does not exist (Bull *et al.*, 1983).

At the conditions applied in this work, the ferric chelates of both EDTA and HEDTA are only present in the monohydroxy form, i.e. according to eqn. (44), and its dimer, and therefore ferric chelate and hydroxide are not formed individually in the above reaction scheme but rather as $Fe^{3+}(OH^-)L^{n-}$. The superoxide species O_2^- is not reactive with the hydroxy forms of the ferric EDTA complex (Brown and Mazzarella, 1987). As this also holds for other hydroxy ferric complexes (Brown and Mazzarella, 1987), it is expected that the hydroxy forms of the ferric HEDTA are also not reactive with superoxide. Therefore, it can be concluded that at the conditions applied here, the backward reaction of eqn. (40) does not occur.

Although hydrogen peroxide may also react with ferric chelates to form back the corresponding ferrous chelates, the reaction of peroxide with ferrous chelate to produce ferric chelate prevails (see: Bull *et al.*, 1983; Borgaard *et al.*, 1971; McClune *et al.*, 1977; Orhanovic and Wilkins, 1967 and Rush and Koppenol, 1987). The difference of the reaction equations (39) to (43) from the scheme of Zang and van Eldik (1991) is the inclusion of the backward reaction of eqn. (40) and the assumption that ν_B^+ not necessarily needs to be equal to 2 because of a possible degradation reaction. Below we will return to this stoichiometric factor.

Assuming steady state conditions for the species O_2^-, H_2O_2 and $Fe^{2+}LO_2$ and taking the water concentration constant, the following reaction rate equation for the ferrous chelate can be derived:

$$-R_B = \left(2+\nu_B^+\right)k_{39}\frac{1+\dfrac{k_{40}/k_{41}C_B}{1+k_{-40}C_P/k_{42}C_B}}{1+k_{-39}/k_{41}C_B+\dfrac{k_{40}/k_{41}C_B}{1+k_{-40}C_P/k_{42}C_B}}C_AC_B \tag{48}$$

in which A stands for oxygen, B for ferrous chelate and P for ferric chelate. The following asymptotic solutions and regimes can be derived from this equation:

A. $\frac{k_{-39}}{k_{41}C_B} << 1$ $\qquad -R_B = \left(2 + \nu_B^+\right) k_{39} C_A C_B$

B. $\frac{k_{-39}}{k_{41}C_B} >> 1$

1. $\frac{k_{40}/k_{41}C_B}{1 + k_{-40}C_P/k_{42}C_B} << 1$ $\qquad -R_B = \left(2 + \nu_B^+\right) \frac{k_{39}k_{41}}{k_{-39}} C_A C_B^2$

2. $\frac{k_{40}/k_{41}C_B}{1 + k_{-40}C_P/k_{42}C_B} >> 1$

a. $\frac{k_{-39}}{k_{40}} >> 1$

1. $k_{-40}C_P/k_{42}C_B << 1$ $\qquad -R_B = \left(2 + \nu_B^+\right) \frac{k_{39}k_{40}}{k_{-39}} C_A C_B$

2. $k_{-40}C_P/k_{42}C_B >> 1$ $\qquad -R_B = \left(2 + \nu_B^+\right) \frac{k_{39}k_{40}k_{42}}{k_{-39}k_{-40}} C_A C_B^2 / C_P$

b. $\frac{k_{-39}}{k_{40}} << 1$

1. $k_{-39}k_{-40}C_P/k_{40}k_{42}C_B << 1$ $\qquad -R_B = \left(2 + \nu_B^+\right) k_{39} C_A C_B$

2. $k_{-39}k_{-40}C_P/k_{40}k_{42}C_B >> 1$ $\qquad -R_B = \left(2 + \nu_B^+\right) \frac{k_{39}k_{40}k_{42}}{k_{-39}k_{-40}} C_A C_B^2 / C_P$

Evidently, the occurrence of regime B2a excludes the occurrence of regime B2b at that temperature and *vice versa.* Also it is apparent that the pH-dependent formation of hydroxy ferric chelates via eqns. (44) to (47) only affects the kinetics of regime B2a2 and B2b2 via C_P, as C_P is effectively zero if the ferric chelate is present in a hydroxy form.

The influence of reactions (39) to (42) on the overall kinetics can be demonstrated as follows. Suppose that reaction (41) is fast relative to the backward reaction of eqn. (39), i.e. $k_{-39} << k_{41}C_{Fe^{2+}L^{n-}}$. Then, irrespective of the rates of reactions (40) and (42),

$Fe^{2+}O_2L^{n-}$ cannot equilibrate with $Fe^{2+}L^{n-}$ and O_2, thus rendering the forward reaction of eqn. (39) to be rate determining. This case is reflected in asymptotic solution A with the reaction scheme being reduced to:

$$Fe^{2+}L^{n-} + O_2 \xrightarrow{k_{39}} Fe^{2+}O_2L^{n-} \tag{49}$$

$$\begin{aligned} Fe^{2+}O_2L^{n-} + \left(1+\nu_B^+\right)Fe^{2+}L^{n-} + 2\,H_2O + \left(2-\nu_B^+\right)OC \\ \xrightarrow{fast} \left(2+\nu_B^+\right)Fe^{3+}L^{n-} + \left(2+\nu_B^+\right)OH^- + \left(2-\nu_B^+\right)DP \end{aligned} \tag{50}$$

where eqn. (50) is the sum of eqns. (41) and (43).

More complicated is the case $k_{-39} >> k_{41}C_{Fe^{2+}L^{n-}}$. Then, all reaction steps have to be considered. However, the formation of hydrogen peroxide through reactions (40) and (42) can still be neglected relative to reaction (41) if reaction (41) is faster than either reaction (40) or (42), thus if

$$k_{41}C_{Fe^{2+}L^{n-}} >> k_{40} \tag{51}$$

or

$$k_{41}C_{Fe^{2+}L^{n-}}C_{Fe^{2+}O_2L^{n-}} >> k_{42}C_{Fe^{2+}L^{n-}}C_{O_2^-} \tag{52}$$

respectively. Again, assuming steady state conditions for the O_2^- species results in

$$C_{O_2^-} = \frac{k_{40}C_{Fe^{2+}O_2L^{n-}}}{k_{-40}C_{Fe^{3+}L^{n-}} + k_{42}C_{Fe^{2+}L^{n-}}} \tag{53}$$

Substitution in eqn. (52) leads to the constraint

$$k_{41}C_{Fe^{2+}L^{n-}} >> k_{40}\Big/\left(1 + k_{-40}C_{Fe^{3+}L^{n-}}/k_{42}C_{Fe^{2+}L^{n-}}\right) \tag{54}$$

Constraint (51) is more severe than the constraint (54) and only one condition needs to be satisfied. So, if reaction (41) is faster than reaction (40), reactions (40) and (42) can be neglected and asymptotic solution B1 is obtained. Then, the reaction proceeds as:

$$2\,Fe^{2+}L^{n-} + O_2 + 2\,H_2O \xrightarrow{k_{39}k_{41}/k_{-39}} 2\,Fe^{3+}L^{n-} + H_2O_2 + 2\,OH^- \tag{55}$$

$$\nu_B^+\,Fe^{2+}L^{n-} + H_2O_2 + \left(2-\nu_B^+\right)OC \xrightarrow{fast} \nu_B^+\,Fe^{3+}L^{n-} + \nu_B^+\,OH^- + \left(2-\nu_B^+\right)DP \tag{43}$$

If both reactions (40) and (42) are fast relative to reaction (41), i.e. $k_{41}C_{Fe^{2+}L^{n-}} << k_{40}\Big/\left(1+k_{-40}C_{Fe^{3+}L^{n-}}/k_{42}C_{Fe^{2+}L^{n-}}\right)$, the formation of hydrogen peroxide through reaction (41) can be neglected. Then, the reaction scheme reduces to the set eqns. (39,40,42,43), which is valid for asymptotic solution B2 with its sub-asymptotes.

For $k_{-1} >> k_2$, reaction (39) is at equilibrium and either reaction (40) or reaction (42) is rate limiting, depending on whether $k_{-40}C_{Fe^{3+}L^{n-}} << k_{42}C_{Fe^{2+}L^{n-}}$ or $k_{-40}C_{Fe^{3+}L^{n-}} >> k_{42}C_{Fe^{2+}L^{n-}}$. The former case results in the asymptote B2a1 with reaction scheme

$$Fe^{2+}L^{n-} + O_2 \xrightarrow{k_{39}k_{40}/k_{-39}} Fe^{3+}L^{n-} + O_2^- \tag{56}$$

$$O_2^- + \left(1+\nu_B^+\right)Fe^{2+}L^{n-} + 2\,H_2O + \left(2-\nu_B^+\right)OC \xrightarrow{fast} \left(1+\nu_B^+\right)Fe^{3+}L^{n-} + \left(1+\nu_B^+\right)OH^- + \left(2-\nu_B^+\right)DP \tag{57}$$

whereas the latter case leads to:

$$Fe^{2+}L^{n-} + O_2 \xleftrightarrow{k_{-39}k_{-40},k_{39}k_{40}} Fe^{3+}L^{n-} + O_2^- \tag{58}$$

$$Fe^{2+}L^{n-} + O_2^- + 2\,H_2O \xrightarrow{k_{42}} Fe^{3+}L^{n-} + H_2O_2 + 2\,OH^- \tag{42}$$

$$\nu_B^+ Fe^{2+}L^{n-} + H_2O_2 + \left(2 - \nu_B^+\right)OC \xrightarrow{\text{fast}} \nu_B^+ Fe^{3+}L^{n-} + \nu_B^+ OH^- + \left(2 - \nu_B^+\right)DP \quad (43)$$

In this scheme reaction (58) is at equilibrium, so:

$$C_{O_2^-} = \frac{k_{39}k_{40}C_{Fe^{2+}L^{n-}}C_{O_2}}{k_{-39}k_{-40}C_{Fe^{3+}L^{n-}}} \quad (59)$$

As reaction (42) is rate limiting, it follows:

$$-R_B = \left(2 + \nu_B^+\right)k_{42}C_{O_2^-}C_{Fe^{2+}L^{n-}} = \left(2 + \nu_B^+\right)\frac{k_{39}k_{40}k_{42}}{k_{-39}k_{-40}}C_{O_2}C^2_{Fe^{2+}L^{n-}} / C_{Fe^{3+}L^{n-}} \quad (60)$$

which is the rate equation for asymptotic solution B2a2, with $\left(2 + \nu_B^+\right)$ the overall reaction stoichiometry.

Returning to the basic equations (39), (40), (42) and (43) governing case B2, we now analyse $k_{-39} << k_{40}$. Now, the velocity of the backward reaction of reaction (40) relative to reaction (42) will determine whether reaction (39) or reaction (40) is rate controlling. If the backward reaction of reaction (40) is relatively slow, reaction (40) cannot reach equilibrium and therefore also reaction (39) cannot reach equilibrium, leaving the forward reaction of reaction (39) to be rate controlling. This is case B2b1, which is the same as already found for asymptotic solution A. If, however, backward reaction (40) is relatively fast, then reaction (42) becomes rate controlling if also backward reaction (39) is fast enough to ensure that reaction (39) is at equilibrium. Thus, asymptotic solution B2b2 is obtained.

The various asymptotic solutions clearly show that the model is capable of handling all the types of concentration dependencies found by the various authors cited in Table II. As no influence of ferric chelate on the reaction kinetics was noticed, the second order dependency on the ferrous chelates of EDTA and HEDTA found in this work can be assigned to the asymptotic solution B1. The same holds for the results of Zang and van Eldik (1990) with respect to the ferrous HEDTA complex. This is further supported by results of Brown and Mazzarella (1987) for other chelates. In light of the high concen-

trations used in this work and the usually lower concentrations used by others as referred to in Table II, it can be concluded that no literature data refer to regime A. Regime B1 implies $\frac{k_{40}/k_{41}C_B}{1+k_{-40}C_P/k_{42}C_B} << 1$. Rewriting this as $\frac{1}{k_{41}C_B/k_{40} + k_{41}C_B k_{-40}C_P/k_{40}k_{42}C_B} << 1$, it follows from $k_{-39}/k_{41}C_B >> 1$ that in regime B1 either $k_{-39}/k_{40} >> 1$ or $k_{-39}k_{-40}C_P/k_{40}k_{42}C_B >> 1$, or both. The latter inequality probably is not the main factor governing the reaction regime because our experiments revealed that the reaction between oxygen and ferrous chelate took place in regime B1 even at very low conversions where C_P/C_B is still very small. More over, superoxide is not reactive with monohydroxy ferric chelate or its dimer, which are the dominant forms of ferric chelate present in solution at the conditions applied in this work. Those who found first order kinetics in ferrous chelate (see Table II) conducted their experiments under conditions that C_P/C_B was different from zero because at least some ferric chelate must have been produced. If the second inequality would govern the reaction regime, no first order dependency could have been observed. So, for all experiments reported in Table II $k_{-39}/k_{40} >> 1$ and the reaction takes place either in regime B1 or in regime B2a, thus excluding regime B2b.

For EDTA, Zang and van Eldik (1990) observed the onset of a change from a first order dependency to a second order dependency on ferrous chelate with increasing ferrous chelate concentration. As they did not experience any influence of the presence of ferric chelate, this can be explained by the change of reaction regime from B2a1 to B1. Brown and Mazzarella (1987) observed a change from first order to second order upon addition of ferric EDTA to their ferrous EDTA containing solutions. This indicates a change in regime from B2a1 to B1 or from B2a1 to B2a2. Above, it was pointed out that a change in the ratio of C_P/C_B is unlikely to change the regime from B2a to B1 and thus the observed change probably was from regime B2a1 to B2a2. This is further supported by the reaction scheme presented by Brown and Mazzarella (1987, see eqns. (3) to (5)) which is rather similar to the scheme derived above for reaction regime B2a2. Therefore, no literature data exist as yet for the ferrous EDTA complex in regime B1. For the ferrous HEDTA complex this regime was observed by Zang and van Eldik (1990), though for low ferrous concentrations only.

Table X. Experimental reaction rate constants at 25 °C and pH about 7.5. Normal printing is used for EDTA and fat printing for HEDTA. The limiting values of k_{-39}/k_{41}, k_{40}/k_{41}, k_{-40}/k_{42} and k_{39} are estimated from the constraints of the asymptotic solutions.

Authors	Order in Fe^{2+}	Concentrations Fe^{2+}	Concentrations Fe^{3+}	regime	$\frac{k_{39}k_{40}}{k_{-39}}$	$\frac{k_{39}k_{41}}{k_{-39}}$ $\times 10^{-2}$	$\frac{k_{39}k_{40}k_{42}}{k_{-39}k_{-40}}$	$\frac{k_{-39}}{k_{41}}$	$\frac{k_{40}}{k_{41}}$	$\frac{k_{-40}}{k_{42}}$	k_{39}
This work	2	< 100	< 100	B1		0.65		>> 100	<< 100		>> 0.65
	2	**< 100**	**< 100**	**B1**		**2.8**		**>> 100**	**<< 100**		**>> 2.8**
Zang and van Eldik, 1991	2	6 - 20	≈ 0	B1		1.51		>> 20	<< 20		>> 0.3
	1	< 3	≈ 0	B2a1	0.23			>> 3	>> 3		
	2	**< 20**	**≈ 0**	**B1**		**9.97**		**>> 20**	**<< 20**		**>> 2.0**
Brown and Mazzarella, 1987	1	2.5	≈ 0	B2a1	0.06			>> 2.5	>> 2.5		
	2	2.5	< 30	B2a2			2	>> 2.5	>> 2.5	>> 0.08	
Bull *et al.*, 1983	1	0.08	= 0	B2a1	0.6			>> 0.08	>> 0.08		
Kurimura *et al.*, 1968	1	< 0.04	< 0.003[a]	B2a1	0.27			>> 0.04	>> 0.04	<< 10	
	1	**< 0.04**	**< 0.003[a]**	**B2a1**	**0.10**			**>> 0.04**	**>> 0.04**	**<< 10**	

a) estimated.

Units: k_{39}, $\frac{k_{39}k_{40}}{k_{-39}}$, $\frac{k_{39}k_{40}k_{42}}{k_{-39}k_{-40}}$ in m^3/mole s; $\frac{k_{39}k_{41}}{k_{-39}}$ in m^6/mole^2 s; $\frac{k_{-39}}{k_{41}}$, $\frac{k_{40}}{k_{41}}$ in mole/m^3; $\frac{k_{-40}}{k_{42}}$ dimensionless; concentrations in mole/m^3.

2. The kinetics of the oxidation of ferrous chelates of EDTA and HEDTA in aqueous solution.

Table X summarises our knowledge of the experimental reaction rate constants at 25 °C and pH = 7.5 as it can be derived from our work and the literature cited in Table II in combination with the constraints that determine the reaction regimes observed. For example, we observed for EDTA $k_{39}k_{41}/k_{-39} = 0.65\times10^{-2}$ m^6/mole^2 s. As the reaction took place in regime B1 with C_B < 100 mole/m^3, it follows from the constraint $k_{-39}/k_{41}C_B >> 1$ that $k_{-39}/k_{41} >>$ 100 mole/m^3 and therefore $k_{39} >>$ 0.65 m^3/mole s.

From Table X, it appears that for EDTA the value for $k_{39}k_{40}/k_{-39}$ is 0.29±0.23 m^3/mole s and for HEDTA 0.1 m^3/mole s (the uncertainty in the latter value is not known). Likewise, it follows that $k_{39}k_{41}/k_{-39}$ is 0.011±0.005 and 0.064±0.036 m^6/mole^2 s for the EDTA and HEDTA complexes, respectively. From these values it can be estimated that for the ferrous EDTA complex the ratio of k_{40}/k_{41} is 26±24 mole/m^3 and for the ferrous HEDTA complex 1.6±0.9 mole/m^3. Since it can be derived from the constraints of the asymptotic solutions and the concentrations used that k_{-39}/k_{41} for both complexes should exceed by far the value of 100 mole/m^3, it follows that $k_{-39}/k_{40} >> 1$ for both complexes, thus validating constraint B2a. The constant k_{39} is much greater than 1 and 3 m^3/mole s for the EDTA and HEDTA complex, respectively.

Above, we concluded that the ratio $k_{40}/k_{41}C_B$ is the main factor governing the change of regime from B1 to B2a. From this ratio, together with the concentrations applied and reaction regimes observed in the references mentioned in Table II, both upper and lower limits for k_{40}/k_{41} were estimated and tabulated in Table X. Indeed, the values of k_{40}/k_{41} as estimated above (26±24 mole/m^3 for the ferrous EDTA and 1.6±0.9 mole/m^3 for the ferrous HEDTA complex) are within all upper and lower limits given in Table X. Although the mean estimated value of k_{40}/k_{41} (= 26±24 mole/m^3) for the EDTA complex is about equal to the upper limit estimated from the data of Zang and van Eldik (1990), see Table X, the latter limit is a very rough estimate because Zang and van Eldik (1990) observed a transition from first to second order in ferrous chelate only. We therefore conclude that our model is consistent with any estimated value of k_{40}/k_{41} from the literature cited in Table II.

The ratio k_{-40}/k_{42} for the EDTA complex can be estimated from the value of the rate constant $k_{39}k_{40}k_{42}/k_{-39}k_{-40}$ as given in Table X in combination with $k_{39}k_{40}/k_{-39}$ = 0.29 m^3/mole s (see above). The result is: $k_{-40}/k_{42} = 0.15$, which again fits within the

estimated limits (see Table X). For ferrous EDTA, k_{42} reportedly is in the range of $(2\text{-}4)\times10^3$ m^3/mole s (Bull *et al.*, 1983; Butler and Halliwell, 1982; Ilan and Czapski, 1977) and k_{-40} ranges from 500 to 2000 m^3/mole s (Buettner *et al.*, 1983; Bull *et al.*, 1983; Butler and Halliwell, 1982; Ilan and Czapski, 1977; Sutton, 1985), leading to an average value of $k_{-40}/k_{42} = 0.4$, which is close to the value calculated above. It can be concluded that also the value for k_{-40}/k_{42} is consistent, both with the model developed above and with the information available from open literature. Combination of $k_{39}k_{40}k_{42}/k_{-39}k_{-40} = 2$ with $k_{39} >> 1$ leads to $k_{-39}k_{-40}/k_{40}k_{42} >> 0.5$. This confirms the above conclusion that the factor is relatively unimportant indeed in changing the reaction regime from B1 to B2 or from B2 to B1. As required, it can be much larger than one only if ferric chelate is present in substantial amounts relative to ferrous chelate.

Unfortunately, less data are available on reaction rate constants of the oxygen-ferrous HEDTA complex system. Buettner *et al.* (1983) measured $k_{-40} = 0.76$ m^3/mole s at 25 °C and it follows (Table X) that $k_{42} >> 0.076$ m^3/mole s and from the ratios $k_{39}k_{40}/k_{-39}$ and k_{-40}/k_{42} that $k_{39}k_{40}k_{42}/k_{-39}k_{-40} >> 0.01$ m^3/mole s, and may well be of the same order of magnitude as for the corresponding EDTA complex.

Finally, the stoichiometric coefficient of reaction equation (43) needs to be discussed:

$$\nu_B^+ Fe^{2+}L^{n-} + H_2O_2 + \left(2 - \nu_B^+\right)OC \xrightarrow{\text{fast}} \nu_B^+ Fe^{3+}L^{n-} + \nu_B^+ OH^- + \left(2 - \nu_B^+\right)DP \qquad (43)$$

with: $1 \le \nu_B^+ \le 2$, OC = Organic Compound and DP = Degradation Product

Usually, and without much discussion, the assumption is that the stoichiometric coefficient ν_B^0 equals 4 (see: Zang and van Eldik, 1991; Brown and Mazzarella, 1987; Asai *et al.*, 1987; Kurimura *et al.*, 1968). Our findings are different, see Figs. 9 and 10. These Figures present ν_B^0, which is equal to $2 + \nu_B^+$, as function of temperature and oxygen concentration. Equation (43) is an overall reaction including more elemental reaction steps. The conversion of hydrogen peroxide to hydroxide anions via hydroxyl radicals, e.g. as shown in eqn. (61) was demonstrated by using specific hydroxyl radical scav-

engers (Gutteridge *et al.*, 1990; Kadiiska *et al.*, 1989, Walling and co-workers, 1970, 1975b).

$$\begin{aligned} Fe^{2+}L^{n-} + H_2O_2 &\longrightarrow Fe^{3+}L^{n-} + OH^- + HO^\bullet \\ Fe^{2+}L^{n-} + HO^\bullet &\longrightarrow Fe^{3+}L^{n-} + OH^- \end{aligned} \qquad (61)$$

Recent work (Rahal and Richter, 1988; Koppenol, 1985; Rush and Koppenol, 1987, 1988), however, indicates that this conversion may also proceed without hydroxyl radicals, e.g. through reaction (62). This conclusion results from the observation that specific hydroxyl radical scavengers do not interfere with the conversion of peroxide thus excluding reaction mechanism (61).

$$\begin{aligned} Fe^{2+}L^{n-} + H_2O_2 &\longrightarrow Fe^{2+}(H_2O_2)L^{n-} \\ Fe^{2+}L^{n-} + Fe^{2+}(H_2O_2)L^{n-} &\longrightarrow 2\,Fe^{3+}L^{n-} + 2\,OH^- \end{aligned} \qquad (62)$$

Sutton *et al.* (1987) found both pathways to be relevant with the first reaction step to be rate determining in both cases (see also: Borggaard et al., 1971; Bull *et al.*, 1983; Sutton, 1985). However, Sutton *et al.* (1987) could not explain why they observed reaction (61) to dominate with t-BuOH as OH-radical scavenger present in solution whereas Koppenol (1985), using the same scavenger, noted reaction (62) to be dominant.

Though it is not known *a priori* by which mechanism hydrogen peroxide reduces to hydroxide, there is general agreement that the intermediate species, i.e. either the $HO^\bullet$ radical or $Fe^{2+}L(H_2O_2)$, is capable of oxidising most organic material (Rahal and Richter, 1988; Rush and Koppenol, 1988; Sahul, 1987; Sutton *et al.*, 1987; Walling and co-workers, 1975a,b) including chelants. The result is that the stoichiometric coefficient decreases with increasing degradation of the chelate due to oxidising side reactions. Thus generally: $1 \leq \nu_B^+ \leq 2$ and therefore $3 \leq \nu_B^0 \leq 4$, see Figs. 9 and 10 for experimental results.

2.7. Conclusions.

For ferrous chelates of EDTA and HEDTA, it has been demonstrated that at ferrous iron chelate concentrations in the range of 10 to 100 or 200 mole/m^3 the reaction between oxygen and ferrous chelate is first order in oxygen and second order in ferrous chelate. In combination with literature data, a reaction model was developed that explains both first order and second order behaviour with respect to ferrous chelate concentration, depending on the relative values of the reaction rate constants. It also explains the deviation of the overall reaction stoichiometry from 4, generally being in between 3 and 4. The reaction rate equation derived from this reaction model describes both our own results and the literature data in all areas investigated so far. In addition, the diffusivities of the iron complexes have also been obtained.

2.8. Nomenclature.

a	Gas-liquid contact area	m^2
C	Concentration	mole/m^3
C^i	Concentration at gas/liquid interface = solubility	mole/m^3
D	Diffusivity	m^2/s
Ea	Activation energy	kJ/mole
E_A	Enhancement factor of oxygen absorption	-
$E_{A\infty}$	Enhancement factor of oxygen absorption at instantaneous reaction	-
F	Faraday's constant = 9.6485×10^4	C/mole
H	Salting-out coefficient	m^3/kmole
He	Henry-coefficient	Pa m^3/s
Ha	Hatta-number	-
J_A	Mass transfer rate of oxygen	mole/m^2 s
J_i	Flux of species i	mole/m^2 s
k	Reaction rate constant	ref. reactions
k_L	Mass transfer coefficient	m/s
k_{21}^0	Pre-exponential reaction rate constant	m^6/mole^2 s
k_{21}	Reaction rate constant found in this work	m^6/mole^2 s
N_A	Amount of oxygen absorbed	mole/m^3

p	Pressure	Pa
R	Gas constant = 8.31441	J/mole K
R_B	Reaction rate of ferrous chelate	mole/m^3 s
t	Time	s
T	Temperature	K
V	Volume	m^3
z	Ion charge	-

Greek symbols

γ	Activity coefficient	m^3/mole
δ	Film thickness	m
δ'	Position of the reaction plane	m
η	Position of the reaction plane	-
λ	Ionic conductivity	m^2/mole Ω
ν	Reaction stoichiometry of rate determining step	-
ν^o	Overall reaction stoichiometry	-
ν^+	Reaction stoichiometry of $Fe^{2+}L/H_2O_2$ reaction	-
Ψ	Electric field force	J/C

Sub- and superscripts

A	Oxygen
B	Ferrous chelate
G	Gas phase
i	Component i
L	Liquid phase
n	Charge of the chelate
P	Ferric chelate
o	At t = 0 (superscript)
o	In water (subscript)
∞	At t = infinite

Chelant types

BDTA	Butylenediaminetetraacetic acid
CyDTA	Cyclohexane-1,2-diaminetetraacetic acid
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EDTP	Ethylenediaminetetrapropionic acid
HEDTA	Hydroxyethylethylenediaminetriacetic acid
MIDA	Methyliminodiacetic acid
NTA	Nitrilotriacetic acid
PDTA	Propylenediaminetetraacetic acid
TPP	Tripolyphosphate

2.9. References.

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Appendix.

Model choice and the influence of the presence of ions on the enhancement of oxygen absorption.

Equation (27) gives the enhancement factor for instantaneous reaction derived from the film model. According to the instationary models of Higbie and Danckwerts, the enhancement factor for instantaneous reactions is given by (Danckwerts, 1970):

$$E_{A\infty} = 1 / \mathrm{erf}(\eta) \tag{A-1}$$

with η defined by:

$$\zeta \cdot e^{(\eta\cdot\zeta)^2} \cdot \mathrm{erfc}(\eta\cdot\zeta) = \frac{C_B}{\nu_B \cdot C_A^i} \cdot e^{\eta^2} \cdot \mathrm{erf}(\eta) \quad \text{with } \zeta = \sqrt{\frac{D_A}{D_B}} \tag{A-2}$$

Figure A-1 shows $E_{A\infty}$ as a function of $C_B/\nu_B C_A^i$ for both the film model, eqn. (27), and the instationary models, eqn. (A-1), together with some of our experimental results obtained in the near-instantaneous reaction regime. Apparently the experimental results are best described by eqn. (27). Application of eqn. (A-1) leads to unrealistically low values of D_B/D_A. Therefore, it is concluded that in the instantaneous reaction regime the enhancement factor according to the film model is appropriate.

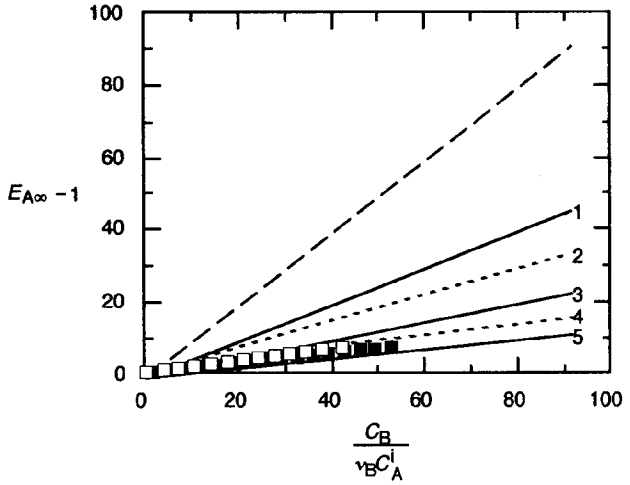

Figure A-1. Comparison of penetration and film model solution for instantaneous reaction. Legend: ■ EDTA; □ HEDTA; — — — $D_B = D_A$, both models predict the same enhancement; ..... instationary model with D_B/D_A = 1/8 (line 2) and 1/64 (line 4); _____ stationary model with D_B/D_A = 1/2 (line 1), 1/4 (line 3) and 1/8 (line 5).

So far we have neglected any possible influence of the presence of charged species on the enhancement. As these influences can be quite substantial, it is imperative to know whether or not they play a role in the present system. The influence of an electric field on the flux of an ion in diluted solution follows from the Nernst-Planck equation (Cussler, 1984):

$$J_i = -D_i\left(\nabla C_i + z_i C_i \frac{F}{RT}\nabla\Psi\right) \qquad \text{(A-3)}$$

in which the first right-hand term accounts for the concentration gradient of species i, with C being its local concentration, and the second right-hand term for the electric force on that species having a charge z. For uncharged molecules this equation reduces to the Fick-equation and for ions to the flux-equation of Vinograd and McBain (1941), provided the assumption of zero-current flow, i.e. $\sum z_i J_i = 0$, can be made. The diffusivity is then replaced by the limiting ionic conductivity λ according to the Einstein relationship (Atkins, 1982; see also: Sherwood and Ryan, 1959):

$$D_i = \frac{RT\lambda_i}{z_i^2 F^2} \qquad \text{(A-4)}$$

Figure A-2 shows typical concentration profiles near the interface (film model) for an uncharged species A absorbing into a liquid, instantaneously reacting with B according to:

$$A + \nu_B B \longrightarrow \nu_P P \qquad \text{(A-5)}$$

or for the reaction of oxygen with ferrous chelates under conditions applied in this work:

$$O_2 + 2\left(Fe^{2+}L^{n-}\right)^{2-n} \xrightarrow{+\,2\,H_2O} 2\left(Fe^{3+}(OH^-)L^{n-}\right)^{2-n} + H_2O_2 \qquad \text{(A-6)}$$

which is the rate controlling step in the oxidation of ferrous chelate by oxygen.

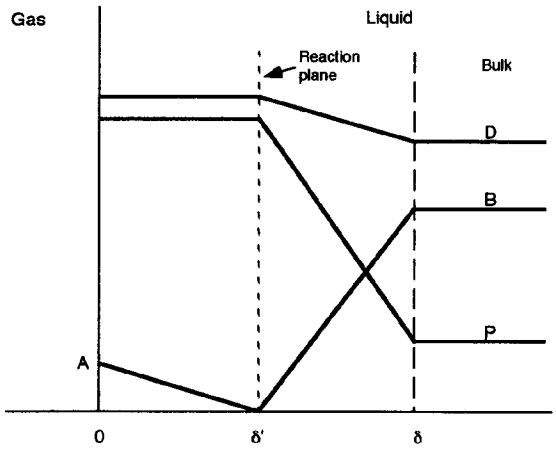

Figure A-2. Typical concentration profiles for a gas A reacting instantaneously with a charged species B to give another charged species C in presence of an unreactive species of opposite charge, D.

2. *The kinetics of the oxidation of ferrous chelates of EDTA and HEDTA in aqueous solution.*

Let species D be the counter-ion of species B. In our case A = oxygen, B = ferrous chelate, P = ferric chelate and D = both sodium and potassium. As the chelates have a negative charge, they primarily interact with positive charged species such as sodium or potassium. The presence of other non-reactive charge carriers will reduce the effect of self-induced electric fields on the mobility of the reactive charge carriers. So ignoring the presence of e.g. chloride will result in an overestimate of influence of a self-induced electric field.

The following boundary conditions apply:

$$\begin{array}{lllll} x = 0: & C_A = C_A^i & C_B = 0 & C_P = C_P^i & C_D = C_D^i \\ x = \delta': & C_A = 0 & C_B = 0 & C_P = C_P^i & C_D = C_D^i \\ x = \delta: & C_A = 0 & C_B = C_{B,bulk} & C_P = C_{P,bulk} & C_D = C_{D,bulk} \end{array} \qquad \text{(A-7)}$$

The concentration gradients follow from:

$$\text{for } 0 \le x \le \delta': \quad \nabla C_A = \frac{-C_A^i}{\delta'} \quad \text{and for } \delta' \le x \le \delta: \quad \nabla C_j = \frac{C_j(\delta) - C_j(\delta')}{\delta - \delta'}, \; j = B,P,D \qquad \text{(A-8)}$$

The actual concentrations are approximated using the method of central differences:

$$\text{for } 0 \le x \le \delta': \quad C_A = \frac{C_A^i}{2} \quad \text{and for } \delta' \le x \le \delta: \quad C_j = \frac{C_j(\delta) + C_j(\delta')}{2}, \; j = B,P,D \qquad \text{(A-9)}$$

From D being inert it follows that $J_D = 0$ and from eqn. (A-3) the influence of the electric field can be expressed in terms of C_D. Imposing the usual conditions of electroneutrality, i.e. $\sum z_i C_i = 0$ (allowing the elimination of C_P) and no net transport of charge, i.e. $\sum z_i J_i = 0$ (allowing the calculation of δ') it follows from the eqns. (A-3), (A-8) and (A-9) that the enhancement factor for instantaneous reaction is given by:

$$E_{A\infty} \equiv \frac{\delta}{\delta'} = 1 + \frac{D_B C_{B,bulk}}{\nu_B D_A C_A^i} \cdot \Phi \qquad \text{(A-10)}$$

2. The kinetics of the oxidation of ferrous chelates of EDTA and HEDTA in aqueous solution.

with:
$$\Phi = 1 - \frac{z_B}{z_D} \cdot \frac{2\alpha C_{D,bulk} + \beta + \sqrt{\beta^2 - 4\alpha\gamma}}{2\alpha C_{D,bulk} - \beta - \sqrt{\beta^2 - 4\alpha\gamma}} \qquad \text{(A-11)}$$

$$\alpha = z_D D_P (z_P - z_D)$$

$$\beta = z_B C_{B,bulk} \left(D_C (z_C - z_P) - D_B (z_B + z_P) \right)$$

$$\gamma = C_{D,bulk} \left(2 z_B C_{B,bulk} (z_B D_B - z_P D_P) - \alpha C_{D,bulk} + \beta \right)$$

For $z_B = z_C = -z_D \neq 0$ equation (A-11) simplifies to : $\Phi = \dfrac{2}{1 + \sqrt{1 + \left(\dfrac{D_B}{D_P} - 1 \right) \cdot \dfrac{C_{B,bulk}}{C_{D,bulk}}}}$

This is the same result as found by Sherwood and Ryan (1959) for the absorption of acetic acid vapour by a sodium hydroxide solution in which $z_B = z_C = -z_D = -1$. This equality also holds for the absorption of oxygen by a ferrous HEDTA solution. For ferrous EDTA solutions, however: $z_B = z_P = -2$. For $D_P = D_B$ equation (A-10) reduces to $\Phi = 1$ and the enhancement of absorption is no longer influenced by charge effects and therefore the charges of B, P and D are unimportant.

For the large iron chelates studied in this work, the diffusion coefficient of the ferrous chelate will be about equal to the diffusion coefficient of ferric chelate whether or not the latter is hydroxylated because the addition of such a small group will hardly have an effect. Also because of the bulkiness of an iron chelate, a change in the charge of the central iron ion will hardly affect the size of the chelate. Therefore, we may assume that for iron chelates also $D_P = D_B$ and thus $\Phi = 1$. So, possible influences of the presence of charged species on the enhancement of oxygen absorption can be neglected. This finding is further supported by the experimental result that the increasing concentration of unreactive charge carriers with increasing ferrous chelate conversion did not affect the enhancement observed. In conclusion, charge effects are presumably absent. Also the good agreement of the experimentally obtained diffusivities with literature data (see main text) supports this conclusion.